“Breaking the Rules”: A Planar Phosphonium Cation

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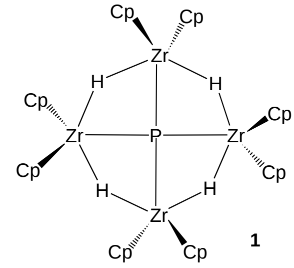
One hundred and twenty five years ago van’t Hoff and Le Bel proposed tetrahedral coordination of carbon atoms.[1–3] This notion, derived from an examination of physical models, was initially conceived to explain the existence of optical and other isomers. Despite the fact that this concept was vehemently attacked at the time, the implications of the three-dimensional arrangement of atoms in molecules soon precipitated work that formed the basic precepts of what was to become the fields of stereochemistry and conformational analysis. The subsequent developments of the Lewis bonding models and classical molecular orbital theory provided a theoretical grounding for the van’t Hoff–Le Bel hypothesis. During the intervening century, this fundamental contribution, made in 1874, was accepted as one of the guiding principles of chemistry. Despite the widespread application of this doctrine in organic and main group chemistry, theoretical predictions in the 1970s suggested the synthesis of planar methane or silane derivatives or their isoelectronic quaternary ammonium or phosphonium analogues might be possible by employing bulky organic or organometallic substituents. While these predictions countered the culture of the day, they threw down a challenging gauntlet to synthetic chemists. Now, almost 30 years after these predictions, Driess and co-workers[4] have achieved the synthesis and characterization of the first planar tetra-substituted phosphonium salt.

Driess and his colleagues have uncovered that reaction of Schwartz’s reagent [Cp_2ZrHCl] and the triphosphenium salt [$P\{P(NMe_2)_3\}_2$][BPh_4] in a 9:1 ratio and in the presence of base results in the formation of the green crystalline product [$P\{Zr(H)Cp_2\}_4$][BPh_4] (**1**) in 11% yield [Eq. (1)].

$$9[Cp_2ZrHCl] \xrightarrow{[P\{P(NMe_2)_3\}_2][BPh_4]/NEt_3} \underset{\mathbf{1}}{[P\{Zr(H)Cp_2\}_4][BPh_4]} \qquad (1)$$

X-ray crystallographic characterization of 1 confirmed the formulation as the phosphonium salt **1**. Moreover, the data establishes the almost ideal square-planar coordination sphere about the central phosphorus atom with Zr-P-Zr angles very close to 90°. Hydrides bridge adjacent Zr atoms forming a nearly planar eight-membered ring that encircles the central P atom.



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Compound **1** represents an unprecedented example of a square-planar phosphonium salt. Use of the highly electropositive metal centers as substituents in **1** are thought to provide the π-acceptor capabilities necessary for delocalization of the π electrons on the phosphorus atom. Zirconium–phosphorus π bonding is known to stabilize unusual geometries, for example, the phosphide complex [$(Cp_2Zr)_2(\mu_2\text{-}Cl)(\mu_3\text{-}P)(ClZrCp_2)$] is trigonal planar at phosphorus.[5] However, compound 1 represents the first case where such Zr–P interactions have been employed to achieve stabilization of an “anti van’t Hoff–Le Bel” configuration. Ab initio calculations support the view that it is electronic factors rather than the steric influence of ancillary ligands that favor the planar phosphorus geometry in **1**.

Previous work by Schmidbaur et al. had described the related per-metalated species [$N\{Au(PPh_3)\}_4$]$^+$ and [$As\{Au(PPh_3)\}_4$]$^+$.[6] However, these species do not exhibit an “anti van’t Hoff–Le Bel” configuration, rather they adopt classical tetrahedral or square-base pyramidal geometries. This is attributable to the poorer π-acceptor properties of the gold fragments and favorable Au···Au interactions. The analogous P-based species is not known although computations also predict a square-pyramidal geometry.[7]

Other compounds adopting an “anti van’t Hoff–Le Bel” configuration, have drawn some recent attention (Scheme 1). Erker and Röttger[8] have recently reviewed such compounds with a particular emphasis on species containing planar-tetracoordinate carbon centers. In a number of these species, the geometry about the carbon center is also stabilized by the presence of electropositive metal centers (e.g. Ti, Zr, Al). Examples of heteroatom “anti van’t Hoff–Le Bel” compounds are less abundant. Several examples of planar tetracoordination exist for boron, while crystals of a phthalocyanine derivative have been found to include a planar silicon atom with a 17% occupancy.[8] Several compounds have been described in which four metal atoms yield a planar oxygen coordination sphere, although no such species have

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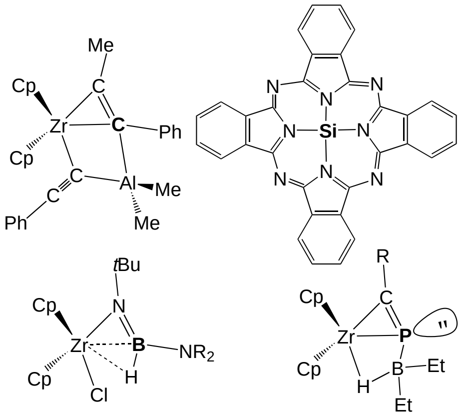

Scheme 1. Selected examples of compounds with atoms in “anti van't Hoff–Le Bel” configurations.

been reported for nitrogen or phosphorus.[8] However, if one considers a lone pair of electrons replacing a fourth substituent, then the phosphaalkyne complex adduct $[Cp_2Zr(RCP)(HBEt_2)]$ reported by Binger et al.[9] can be considered to contain a phosphorus atom in an “anti van't Hoff–Le Bel” configuration.

The strategy employed by Driess et al.[4] in the isolation of **1** may well have broad implications. Theoretical computations suggest that analogous “anti van't Hoff–Le Bel” geometries for SiR_4 and $[AlR_4]^-$ ($R = Zr(H)Cl_2$) may well be accessible. Similar calculations for ER_4 ($E = B^-, C, N^+$) infer a preference for a distorted tetrahedral geometry. However, it may be that other electropositive organometallic fragments will provide the requisite π-delocalization permitting access to a broader variety of compounds in “anti van't Hoff–Le Bel” configurations. While the preparative routes to other compounds containing these unusual geometries remains a synthetic challenge, this breakthrough prompts new and important fundamental questions regarding the effect of distorted geometries on the reactivity and reaction pathways. The discovery of this class of planar-tetracoordinate compounds does not supplant the 125-year-old notions of van't Hoff and Le Bel, rather, it describes exceptions to the “rules”, broadening our understanding of molecular structure. Perhaps more importantly, these efforts demonstrate that even long-standing tenets of a discipline must be questioned in an effort to more fully understand the fundamentals of the science.

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How Many Networks Can Be Made from Four-Coordinate Atoms?

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In diamonds tetrahedrally coordinated atoms form a recurring, three-dimensional network. The same kind of network is found in cristobalite, with Si-O-Si groups taking the place of C–C bonds. A large number of other networks which consist of similarly joined tetrahedral building units are known among the polymorphs of SiO_2 and H_2O and especially among the zeolites.[1] In the network we can discern knots (Si atoms), edges (Si-O-Si bonds), and enclosed voids. The voids can be treated as tiles; a zeolite structure is then a three-dimensional recurring tiling. The tiles can have different shapes. For example, cubes, hexagonal prisms, β-cages (octahedra with cut vertices), and several others occur in zeolites. Every knot is joined with four other knots in a first sphere; in a second (and third, etc.) sphere, there may be different numbers of knots and they can be connected in different ways. For this reason, different kinds of knots can exist. Depending on the number of different kinds of knots the network is called uninodal, binodal, etc.

In two dimensions, there exist eleven different uninodal tilings, which already have been described by Johannes Kepler,[2] and 508 binodal tilings.[3] A procedure to calculate the numbers of possible tilings has been developed by the mathematician Dress and co-workers.[4, 5] Thus, the number of 508 was confirmed[6] and the number of possible trinodal two-dimensional tilings was calculated to be 16774.[7] Now the same research group has extended the procedure to three-dimensional tilings,[8] a fact that was even acknowledged in the daily newspapers. An essential part of the calculations deals with “Delaney symbols”. These allow the neighborhood of a tile to be designated in a concise way. The numbering of all recurring tiling amounts to the numbering of Delaney symbols.

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